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BL2F

Transforming Black Liquor to Biofuel

Research and Innovation Action

H2020-LC-SC3-2019-NZE-RES-CC

D3.2 - Report on IHDO

WP3 - Task 3.2.1

30.1.2024

Lead Beneficiary: VTT

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This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Grant Agreement n°884111.

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Document Information

Grant agreement	884111
Project title	Black Liquor to Fuel by Efficient Hydrothermal Application integrated to Pulp Mill
Project acronym	BL2F
Project coordinator	Prof. Dr. Tero Joronen
Project duration	1st April 2020 – 31st March 2024 (48 Months)
Related work package	WP 3 - Upgrading and application testing
Related task(s)	Task 3.2.1 - IHDO
Lead organisation	VTT
Contributing partner(s)	PSI, Ranido
Due date	31.1.2024
Submission date	30.1.2024
Dissemination level	PU

History

Date	Version	Submitted by	Reviewed by	Comments
17.1.24	v1.0	S. Rautiainen	Judit Sandqvist, Ursel Hornung	Issued for comments
29.1.24	v2.0	S. Rautiainen		Final version

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Abbreviations and acronyms

Acronym	Description
AC	Activated carbon
BL	Black liquor
DI	Deionised
DMDS	Dimethyldisulfide
DO	Deoxygenated
DoD	Degree of deoxygenation
HDO	Hydrodeoxygenation
HTL	Hydrothermal liquefaction
IHDO	Integrated hydrothermal hydrodeoxygenation
IHTL	Integrated hydrothermal liquefaction
IE	Isoeugenol
M	Model compound
MC	4-methylcatechol
RT	Room temperature
SCW	Supercritical water
WHSV	Weight hourly space velocity
WSP	Water soluble products

Executive Summary

This report reviews the work done on the integrated hydrothermal hydrodeoxygenation (IHDO), which is the first hydrotreatment step in the BL2F concept. According to the process concept, the aim of the first HDO step is to increase the stability of the fuel intermediate and to reduce the oxygen content to enable transportation and further upgrading at the oil refinery. The BL-derived HTL-product has a high water content, and therefore the focus of the work was on the stability and activity of the HDO catalysts under hydrothermal conditions. The catalysts were tested both in batch experiments and under continuous flow conditions. Due to the unavailability of the BL-derived HTL-product from TAU, the hydrothermal HDO experiments were conducted using model compounds and lignocellulosic HTL biocrude from Aarhus University. Isoeugenol and 4-methylcatechol were selected as the model compounds based on the results of HTL experiments from KIT.

The main findings in the IHDO can be summarised as follows:

1) Supercritical conditions in a continuous flow system are very challenging for catalyst stability. While sulfided NiMo catalysts on different support materials were successfully employed in batch experiments at SCW, extensive leaching of the active metals was observed in continuous flow experiments with the same catalysts.

2) Ruthenium on carbon is a promising catalyst for HDO in SCW conditions, and furthermore, it's stable with a sulfur-containing feed.

3) The main products of hydrothermal HDO of the model compounds were phenols and cresols, indicating that full deoxygenation of the phenolics is very challenging in aqueous conditions.

4) Hydrotreatment of the HTL biocrude gave rather low yields of the upgraded bio-oil (40-60 wt%), and significant amounts of coke formed especially in SCW (up to 40 wt%). However, the Aarhus biocrude used in the experiments was rather aged, and therefore further studies using the BL-derived HTL product would be required to confirm the observations of the work.

Keywords

Black liquor, Hydrodeoxygenation, HTL, Biocrude, Catalysts

1. Introduction

The Black Liquor to Fuel project introduces a concept for valorising black liquor (BL), an underutilised side stream from Kraft pulp mills, into marine and jet fuels. The process uses integrated hydrothermal liquefaction (IHTL) under supercritical conditions to separate the cooking salts into a brine fraction and to simultaneously produce HTL-product, which contains water along with majority of the organic fraction of the black liquor (Figure 1). The HTL-product requires further upgrading by hydrotreatment to increase its stability and to improve the quality of the produced fuel intermediate. This first upgrading process, called integrated hydrothermal hydrodeoxygenation (IHDO) is integrated into the pulp mill and the IHTL process. As a product, a fuel intermediate stable for transportation or even a drop-in fuel component suitable for marine fuels is obtained. Further upgrading of the intermediate (2nd stage HDO) is planned to be carried out at an oil refinery.

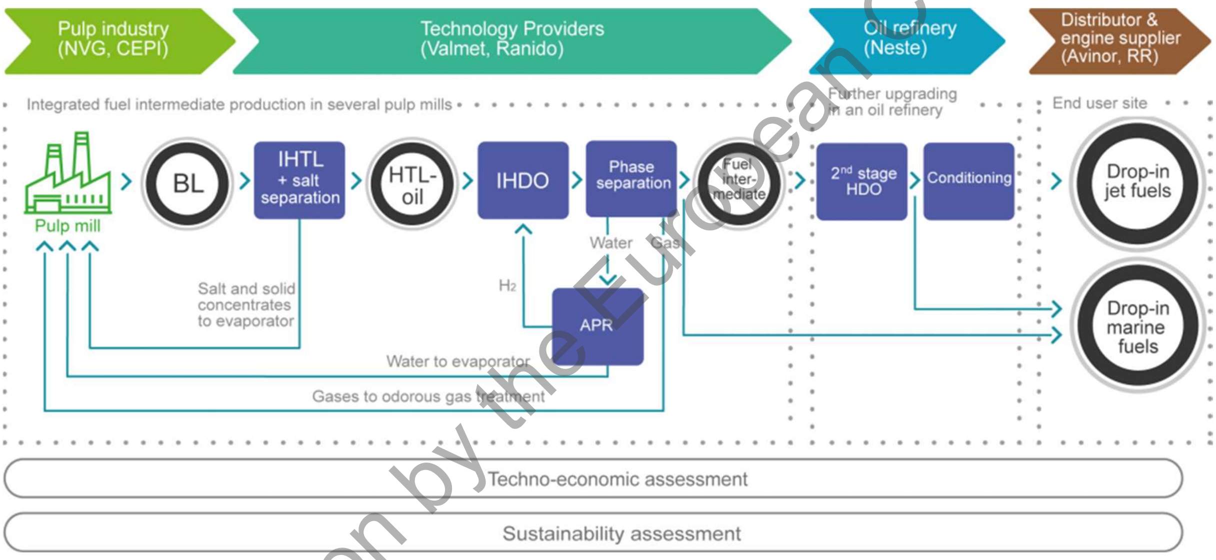


Figure 1. Scheme of the BL2F process concept.

This report covers the work done in task 3.2.1 on the hydrothermal hydrodeoxygenation of HTL-oil and related model compounds in batch and continuous flow experiments. The aim of the task was to evaluate the effect of HDO catalysts and reaction conditions, i.e. the use of supercritical water as medium in the hydrodeoxygenation.

Hydrothermal conditions are very challenging for the stability of the catalyst. Therefore, alongside this task, the Catalyst development task 3.1 concentrated on the development and testing the stability of the catalysts and catalyst support materials under the supercritical water conditions. The results from the catalyst development are reported in D3.1. The most stable catalysts were selected for this task to study their performance in the HDO experiments.

2. Feedstock and model compounds

According to the BL2F process concept, the feedstock for the IHDO process is the HTL-product which contains most of the organic carbon of the BL along with an aqueous phase containing residual salts and sulfur compounds. The intended feedstock for the IHDO studies was the HTL-product from the TAU pilot reactor. However, we started the work in T3.2 using model compounds, but due to the delays in commissioning of the pilot and the consequent unavailability of the real feed. Most of the work done in this task was done using model feedstock. As there is a limited number of studies on the hydrothermal HDO, especially in supercritical water (SCW), the model compound studies serve as an important way of investigating the catalyst performance in the hydrodeoxygenation of the relevant functional groups as well as the catalyst stability under the desired process conditions. In this context, having model feedstock considerably increases the understanding of the performance of the catalyst, and allows revealing part of the chemical pathway yielding hydrogenated/ deoxygenated products.

The composition of the BL-derived HTL-oil was studied by KIT after experiments in batch mode (D1.2). The black liquor has a high content of aromatics which originate from the lignin in the lignocellulose. Based on the results from KIT, the HTL-oil contains monomeric compounds, oligomers as well as high molecular weight lignin. The main aromatic components of the BL-derived HTL-oil are catechols and methoxy-group containing phenols, such as syringol and guaiacol. To simulate the composition of the HTL-oil, we selected three monomers as model compounds (Figure 2). Isoeugenol (IE) was selected due to its multiple functionalities: phenolic hydroxyl group, methoxy group and an aliphatic double bond. Furthermore, isoeugenol is a commonly used model compound of bio-oils which enables easier comparison with other studies. 4-methylcatechol (MC) was selected to represent catechol structure with added complexity from the methyl group. Finally, to study the cleavage of C-C bonds which are abundant in the higher molecular weight lignin after Kraft pulping, diphenylmethane was selected as a dimeric model compound. All of these model compounds were used in the batch experiments at VTT, whereas the continuous flow experiments at PSI were conducted using isoeugenol as a multifunctional model compound.

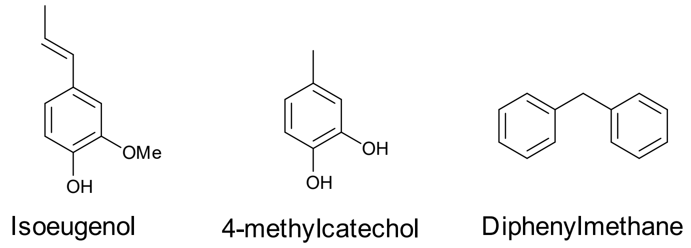


Figure 2. The model compounds used in the hydrothermal HDO experiments.

As the TAU pilot plant failed to produce the HTL-product in sufficient quantity and quality for testing the IHDO, we sought for alternative sources of HTL-oil to complete the work on the hydrothermal HDO. As BL-based HTL-oil was not available from other sources, HTL-oil made by Aarhus University using pine as a feedstock was selected as the feedstock.

Table 1 gives an overview of the experiments carried out on the model compounds and HTL biocrude. Overall, about 80 batch experiments were carried out at VTT and 25 experiments in continuous mode at PSI.

Table 1. Overview of the IHDO experiments

Feedstock	Reactor type	Catalysts	Temperature range	Hydrogen source	Partner
Model compounds: isoeugenol, 4-methylcatechol, diphenylmethane	Batch	Sulfided NiMo	350-380 °C	5-30 bar H_2	VTT
HTL biocrude (pine-based biocrude from Aarhus University)	Batch	Sulfided NiMo, Ru/AC	320-380 °C	5-30 bar H_2	VTT
Model compounds: isoeugenol, isopropanol (hydrogen formation)	Continuous flow	Sulfided Ru/AC	365 – 415 °C	*In situ* (isopropanol)	PSI

3. Catalyst development

Sulfided catalysts containing non-noble metals like nickel, molybdenum and cobalt are widely used for hydrotreating processes including hydrodeoxygenation. Existing commercial processes include the HDO of fatty acids and triglyceride feedstocks. Considering HTL-product from the BL2F process, the advantage of these catalysts is the tolerance towards sulfur in the feed. Noble metal catalysts have also shown high activities in HDO of biobased feedstocks. For instance, comparison of HDO activity of different commercial noble and non-noble metal catalysts in subcritical water showed that noble metals Pt and Ru were very efficient in upgrading of duckweed biocrude (Zhang, 2014).

Hydrothermal conditions are especially demanding for the catalyst stability, both for the support and the active metal. Therefore, the catalyst development in Task 3.1 focused on the stability of the catalysts and the supports under the supercritical water conditions. The stability of the catalysts and supports prepared by Ranido was tested in batch and continuous mode at VTT and PSI, respectively. While the results of the catalyst development are reported in confidential report D3.1, a short summary of the work is presented here as the basis of the HDO experiments.

The HDO of intermediate HTL-oil (coming from conversion of black liquor) was planned to proceed under SCW conditions, therefore, the catalyst selection was started with a selection of supports that can withstand the SCW conditions. The materials prepared by Ranido were tested at VTT by subjecting the material to supercritical water conditions at 380 °C for 2 hours. The suitable carriers were identified from batch experiments carried at VTT based on crush strength and nitrogen physisorption measurements (Table 2).

Out of the tested supports, α-alumina, rutile and activated carbon showed acceptable stability in SCW. Furthermore, zirconia was selected for catalysts preparation and to test its performance. These supports were impregnated with nickel and molybdenum oxides and sulfided prior to use. Based on the results of the stability and HDO experiments, the catalysts were further developed and new samples were prepared. The textural characteristics of the resulting samples are summarised in Table 3. The elemental compositions of the samples based on XRF analyses are summarised in Table 4.

Table 2. Characterisation of catalyst carriers before and after batch SCW treatment.

Sample	Sample description	Crush strength (N)		BET surface (m^2/g)		SCW stable
		Before	After	Before	After	
CAR-01	α -Al_2O_3	100	101	1.8	2.2	**yes**
CAR-02	TiO_2 (rutile)	53	46	3.6	3.7	**yes**
CAR-03	m-ZrO_2	62	11	56	47	**no**
CAR-04	m-ZrO_2	27	4	102	47	**no**
CAR-05	m-ZrO_2	34	15	65	46	**no**
CAR-06	β-SiC	234	125	27	28	**yes***
CAR-07	activated carbon	140	134	890	798	**yes**
CAR-08	m-ZrO_2	69	11	40	47	**no**
CAR-09	m-ZrO_2	128	111	14	13	**yes**

* Decrease in a crush strength

Table 3. Textural characteristics of the as-prepared catalysts.

				Nitrogen physisorption data			
Sample	**Sample description**	**Batch**	**Granulate size (mm)**	**BET surface (m^2/g)**	**Pore volume (mm^3/g)**	**Average pore diameter (nm)**	**Hg pore volume (mm^3/g)**
BLF-01	NiMo/α-Al$_2$O$_3$ CAR-01 impreg. NiMo, oxide form	M201102	<0.4	3.5	12.3	13.9	177
BLF-02	NiMo/TiO$_2$ CAR-02 impreg. NiMo, oxide form	M2109304	0.2-0.4	6.2	18.1	11.6	141
BLF-03	NiMo/ZrO$_2$ CAR-03 impreg. NiMo, oxide form	M2110014	0.2-0.4	26.6	101	15.3	127
BLF-07	NiMo/AC CAR-07 impreg. NiMo, oxide form	M21121608	0.4-0.8	759	341	1.8	113
BLF-07a	NiMo/AC CAR-07 impreg. NiMo, oxide form	M22061708	0.4-0.8	908	424	1.9	233
BLF-10	NiW/AC CAR-07 impreg. NiW, oxide form	M23041408	0.4-0.8	940	452	1.9	208

Table 4. XRF analyses of the as-prepared catalysts.

Sample	**Granulate size (mm)**	**Na$_2$O (%)**	**Al$_2$O$_3$ (%)**	**SiO$_2$ (%)**	**P$_2$O$_5$ (%)**	**K$_2$O (%)**	**CaO (%)**	**TiO$_2$ (%)**	**NiO (%)**	**ZrO$_2$ (%)**	**MoO$_3$ (%)**	**HfO$_2$ (%)**	**WO$_3$ (%)**
BLF-01	<0.4	0.05	70.81	0.02	2.0	0.02	0.05	0.00	3.78	0.00	23.2	0.00	0.00
BLF-02	0.2-0.4	0.00	0.00	0.00	3.0	0.00	0.02	59.3	6.45	0.03	31.0	0.00	0.00
BLF-02	0.4-0.8	0.00	0.01	0.00	2.7	0.00	0.02	63.1	5.89	0.03	28.12	0.00	0.00
BLF-03	0.2-0.4	0.00	0.00	0.00	2.7	0.00	0.00	0.04	5.7	63.8	26.5	1.2	0.00
BLF-03	0.4-0.8	0.00	0.13	0.00	2.4	0.00	0.00	0.05	5.23	65.2	25.6	1.2	0.00
BLF-07	0.4-0.8	0.04	0.03	0.18	1.4	0.16	0.07	0.01	4.1	0.02	18.7	0.00	0.00
BLF-07a	0.4-0.8	0.07	0.02	0.17	0.62	0.79	0.04	0.00	1.3	0.00	6.2	0.00	0.00
BLF-10	0.4-0.8	0.03	0.02	0.12	0.03	0.27	0.06	0.00	1.8	0.01	0.00	0.00	9.45

Although the resulting NiMo catalysts (BLF-01, BLF-02, BLF-03 and BLF-07) worked well after sulfidation in the batch tests under SCW on model compounds, the continuous flow tests under SCW conditions resulted in significant losses of NiMo from the catalyst surface (Table 5). To improve the stability of the catalysts, several modifications were made to the impregnation methods, e.g. impregnation procedure change (CAR-02 impregnated with three different NiMo formulations), lowering of NiMo concentrations (BLF-07a) or switching to a NiW catalyst (BLF-

10 supported on activated carbon). However, these modifications did not help to prevent the leaching of the metals.

Because of unsatisfactory stability of the NiMo and NiW samples, a ruthenium on activated carbon (Ranido standard product RCAT®-8830) was introduced. Properties of RCAT®-8830 are shown in Table 6. Finally, this catalyst was concluded to be stable under SCW under both batch and continuous mode in both metallic and sulfided form.

Table 5. Results of catalyst stability tests in continuous flow setup.

Sample	Loss of Mo (%)	Loss of Ni (%)
BLF-02	>95	60
BLF-02-S	60	40
BLF-03	90	55
BLF-07	80-90	40-50
BLF-07-S	40-70	10-30
BLF-07a-S	70	50
BLF-07a-S*	60	40

* 1000 ppm DMDS

Table 6. Properties of employed ruthenium on activated carbon.

Sample	Lot	Granulate size (mm)	Bulk density (kg/m^3)	Moisture (%)	Ru content (dry mass) (%)
RCAT®-8830	G230130R	0.4-0.6	680	48	4.75

4. Batch experiments

4.1. Experimental

4.1.1. Materials

The model compounds isoeugenol (>98%, mixture of *cis*- and *trans*), 4-methylcatechol (>95%) and diphenylmethane (99%) were supplied by Merck and used as received. For GC calibration, 4-propylphenol (>99%, TCI), p-cresol (>98%, Merck) and propylcyclohexane (>98%, TCI) were used as received.

4.1.2. Reactor setup

The stability tests, catalyst sulfidation and HDO experiments were carried out in a 1 L autoclave by Autoclave Engineers equipped with a mechanical stirrer, temperature and pressure sensors. The reactants were measured into an inner liner which was placed inside the reactor. After the reaction, cooling of the reactor was aided by air flow on the outside of the reactor. The heating and cooling times were about 80-90 minutes depending on the reaction temperature.

4.1.3. Catalyst sulfidation

For the catalyst sulfidation, 10 g catalyst, 100 ml n-hexane and 5 ml dimethyldisulfide was added in the reactor, the reactor was sealed and flushed three times with nitrogen. 30 bar hydrogen gas was loaded at room temperature, and the sulfidation was run at 350 °C for 4 h. The sulfided catalyst was stored under n-hexane.

4.1.4. Model compound experiments

For the model compound experiments, the catalyst and 1 g of each model compound was added into the reactor along with 125 ml of deionised water. The reactor was then sealed and flushed with nitrogen before pressurising with hydrogen to the desired pressure. The experiments were run at 2 h at the target temperature, after which the reactor was cooled to room temperature. A gas sample was taken into a gas bag for analysis with GC. The reaction mixture was filtered through a filter paper into a separation funnel to separate the catalyst. The catalyst residue was washed with 10 ml isopropanol followed by 50 ml ethyl acetate. The aqueous phase was separated and further extracted with 50 ml ethyl acetate. Both the aqueous and organic phase were analysed by GC-MS.

4.1.5. HTL-oil experiments

The HTL pine biocrude obtained from Aarhus University was a rather old sample which has been stored at room temperature. Therefore, the biocrude was very viscous and hard to handle. To enable easier processing, the solids were removed by dissolving the biocrude into isopropanol, filtering and removing the solvent by rotary evaporator, and the resulting pretreated biocrude was used as such for the experiments.

For a typical HDO experiment, 28 g pretreated biocrude, 2.8 g catalyst (10 wt%) and 128 ml deionised water were measured into the reactor. The reactor was loaded with hydrogen to the desired pressure and heated to the desired temperature while stirring with mechanical stirrer.

4.1.6. Analytical methods and calculation of results

4.1.6.1. Gas chromatography

The products from the model compound experiments were analysed from both the organic phase and the aqueous phase using 1-butanol as internal standard by an Agilent 7890A GC equipped with a J&W HP-Innowax column (60 m x 250 μm x 0.25 μm) and FID and 5977B MS detectors. The oven temperature program was as following: initial temperature of 60 °C was held for 1 min, then the column was heated to 260 °C at a rate of 3 °C/min and kept at this temperature for 10 min. The FID signals were used for quantitation after calibration and MS for identifying the products. Calibration was done for the model compounds as well as for major products 4-propylphenol, p-cresol and propylcyclohexane. The concentrations of other products were estimated using response factors for the closest calibrated compound.

Water soluble compounds in the aqueous phase after biocrude upgrading were analysed using similar GC-MS method in selected samples.

The gas samples were analysed for non-condensable gases and light hydrocarbons using an Agilent 490 micro-GC equipped with four columns (10 m Molsieve-5A, 10 m Poraplot-U, 10 m Al_2O_3 KCl and 8 m CP-Sil 5 CB) and four TCDs. The molar amounts of gas-phase products were calculated using the ideal gas law by estimating the gas volume in the reactor.

4.1.6.2. Analysis of biocrude

The elemental composition (CHN) of the biocrude was analysed before and after upgrading. The organic carbon content in the aqueous phase after biocrude upgrading was analysed using a Shimadzu TOC-VCPH. Water content of the samples was measured by Karl Fischer titration. Oxygen content was calculated as difference.

4.1.6.3. Calculation of results

Conversion of each model compound (M) at reaction time *t* was determined from the following equation (1).

$$X_t = \left(\frac{n_{M_0} - n_{M_t}}{n_{M_0}}\right) x\ 100\% \qquad (1)$$

Due to the high number of products from the experiments, the products were grouped according to their functionality into phenols, deoxygenated aromatics, aliphatic oxygenates and cycloalkyls. The selectivity to each product group *pg* was calculated in mol% according to equation (2).

$$S_{pg} = \frac{n_{pg}}{n_{all\ products}} x\ 100\% \qquad (2)$$

Carbon balance of the model compound experiments was calculated based on the amount of detected products (3).

$$C_{\%} = \frac{n_{products}}{n_M} x\ 100\% \qquad (3)$$

Degree of deoxygenation was calculated based on the decrease of oxygen content (wt%) in the products compared to the starting materials.

$$DoD_{wt\%} = \frac{m_{O(M)} - m_{O(products)}}{m_{O(M)}} x\ 100\% \qquad (4)$$

4.2. Results

4.2.1. Model compound experiments

The aim of the model compound experiments was to compare the different catalysts and the effect of the reaction conditions on the deoxygenation of the model compounds. All four catalysts used in the model compound experiments were sulfided nickel molybdenum catalysts with different supports: titania, zirconia, α-alumina and activated carbon. The catalysts were selected based on the stability tests in batch mode performed at the start of the project. The reaction parameters studied were temperature (350-380 °C) and hydrogen loading (2-30 bar at RT). The conditions were selected so that the critical point of the water (374 °C, 221 bar) was reached at the highest temperatures and pressures. The lower points were included to compare the supercritical conditions to subcritical conditions. Design of experiments (full factorial) was utilised in the planning, though we were unable to load the maximum hydrogen pressure at the maximum temperature due to limits of the reactor setup. In all experiments, the reaction time was 2 h, and the amount of the catalyst and the model compounds was kept unchanged. After the experiments, the aqueous phase was extracted with ethyl acetate to recover the products. Both the organic and aqueous phase were analysed by GC-MS. However, the amount of organic compounds detected in the aqueous phase was negligible, and therefore the results presented below are based solely on the analysis of the organic phase. Numerous compounds were identified in the product mixture and to facilitate the interpretation of the results, the products were grouped into phenols, deoxygenated aromatics, aliphatic oxygenates and cycloalkyls (Figure 3). Analysis of the gas phase was done for the selected experiments to investigate the amount of carbon in the gaseous products.

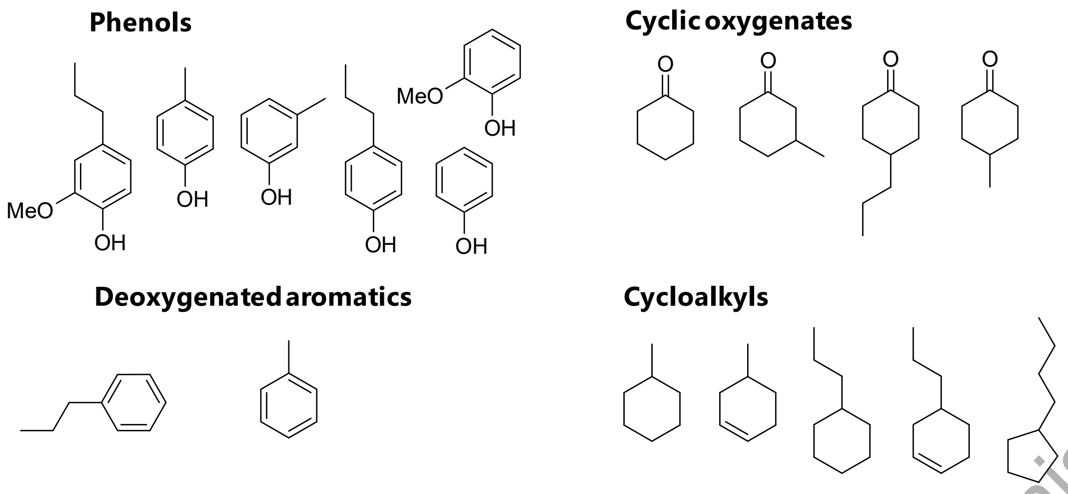


Figure 3. Examples of the products identified after the HDO experiments.

The results of the experiments with different catalysts are presented in the following Figures 4-7. The pressure at the reaction temperature is indicated in the graphs along with the experiments, where supercritical conditions (SCW) were reached. The graphs depict the substrate conversion, carbon balance, degree of deoxygenation and the selectivity to different product groups. Furthermore, the extent of cracking of the propylbenzene backbone in IE was calculated by the yield of C9 products compared to IE. No conversion of diphenylmethane was observed in the experiments with the model mixture or in control experiments with only diphenylmethane. Therefore, the dimer is omitted from the results.

The results of the HDO experiments with sulfided NiMo/TiO$_2$ (BLF-02-S) are presented in Figure 4. Full conversion of IE was observed in all experiments, which was expected since the aliphatic double bond is easily hydrogenated. The conversion of MC varied between 25-100 mol%; higher hydrogen pressures and temperatures were needed to reach high conversion, and full conversion was only reached at SCW using the highest hydrogen loading. Carbon balance, calculated based on the moles of products observed in GC, varied between 38-55%, which is in line with those reported previously by e.g. Lindfors (2019). In all of the experiments, phenols accounted for more than 75 mol% of the products; cresols and propylphenols were the most abundant phenols observed. The second most abundant product group was cyclic oxygenates, which contained several alkyl-substituted cyclohexanones. The selectivity depended heavily on the reaction conditions; up to 20% cyclic ketones was observed using 30 bar H$_2$ loading at 350 °C. The amount of deoxygenated products was rather low in all of the experiments. Deoxygenated aromatics, such as propylbenzene and toluene, were obtained with only up to 3% selectivity. Upon increasing the temperature and hydrogen loading, further hydrogenation led to formation of cycloalkyls in up to 6% selectivity. Despite the low amounts of fully deoxygenated products, the overall degree of deoxygenation showed strong dependency on both the temperature and hydrogen loading, following a similar trend to the conversion of MC. At low H2 loading and 350 °C temperature, a negative DoD was observed. This could be explained by the low MC conversion, and also by the extensive cracking of the IE C9 backbone;

only 4 mol% of C9-products were observed compared to the starting IE. The highest DoD observed was 44% at the highest temperature and hydrogen loading.

The sulfided NiMo/ZrO_2 (BLF-03-S) was slightly more active in the model compound HDO than the titania-supported catalyst, even though the trends were very similar (Figure 5). The main differences were the slightly higher MC conversion; full conversion was obtained already at 350 °C with a high hydrogen loading. Furthermore, the catalyst showed higher tendency towards deoxygenation of the model compounds; cycloalkyls and deoxygenated aromatics were observed in several experiments. Comparison of the experiments in subcritical and supercritical regime showed that similar results (conversion, DoD) could be obtained at lower temperatures with higher hydrogen loadings. The selectivity to aliphatic products was higher at the lower temperature, probably due to the higher availability of hydrogen.

The catalysts supported on α-alumina and activated carbon were studied using the minimum and maximum temperatures and hydrogen loading, resulting in four experiments with each catalyst. Out of the four catalysts tested, the sulfided NiMo/α-Al_2O_3 (BLF-01-S) showed the least activity in HDO of the model compounds (Figure 6). The highest MC conversion and DoD were 88% and 27%, respectively, and the values were obtained in SCW at 380 °C and 15 bar hydrogen loading. Accordingly, very little deoxygenated compounds were detected with the catalyst. In addition to the analysis of the liquid phase, the gas phase was analysed for each experiment, and the results are presented in

Table 7. Up to 4.3% of the carbon of the model compounds was detected in the gas phase products, the most abundant being carbon dioxide and methane.

Compared to the metal oxide-supported catalysts, the sulfided NiMo/AC (BLF-07-S) showed higher activity both in terms of MC conversion and DoD (Figure 7). At 350 °C and 5 bar hydrogen loading, DoD was already at 20%, while the other catalysts gave zero or negative values. At harsher conditions, the DoD values stabilised at around 40%, both in subcritical and supercritical experiments. Despite the high conversions, the selectivity to deoxygenated or aliphatic compounds was low, only up to 5%. Interestingly, the carbon-supported catalyst also showed less tendency towards cracking, and consequently increased selectivity to C9 products was observed compared to the metal-oxide supported catalysts. In the gas phase, up to 8% carbon products was detected.

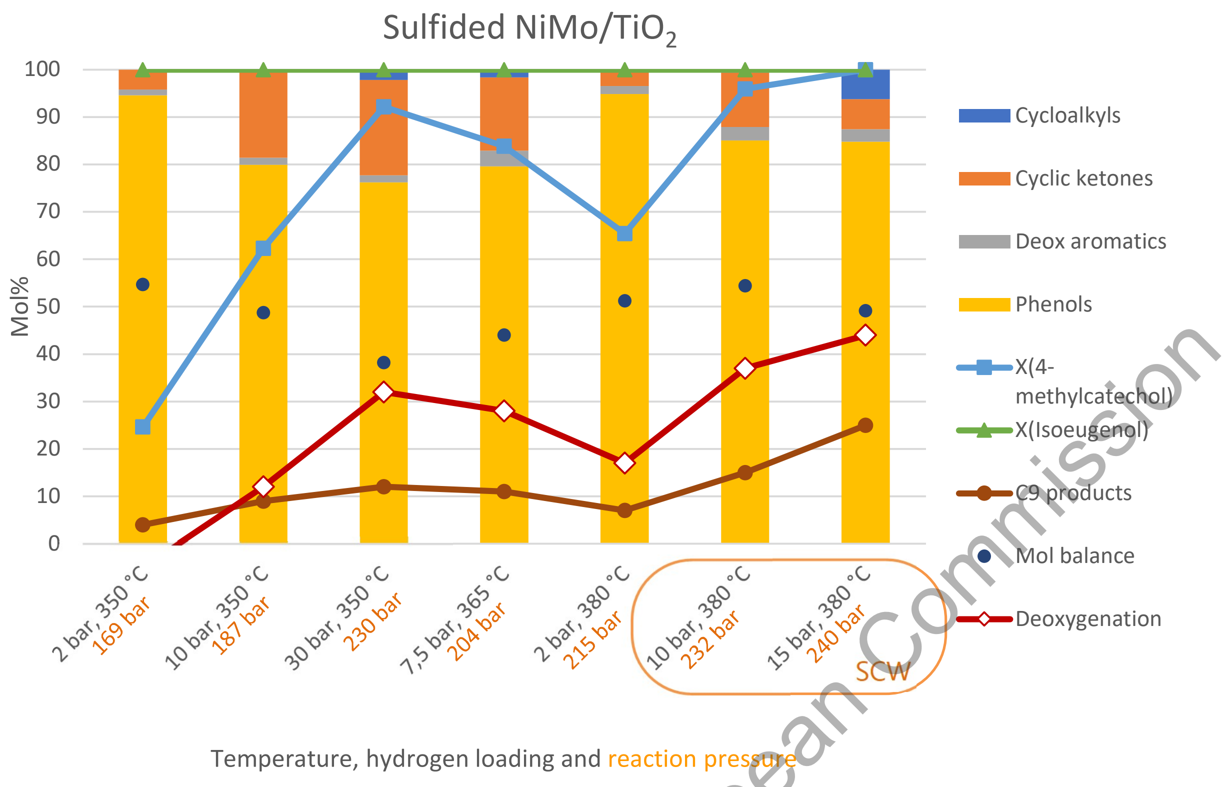


Figure 4. Effect of reaction conditions on model compound HDO with sulfided NiMo/TiO$_2$ (BLF-02-S).

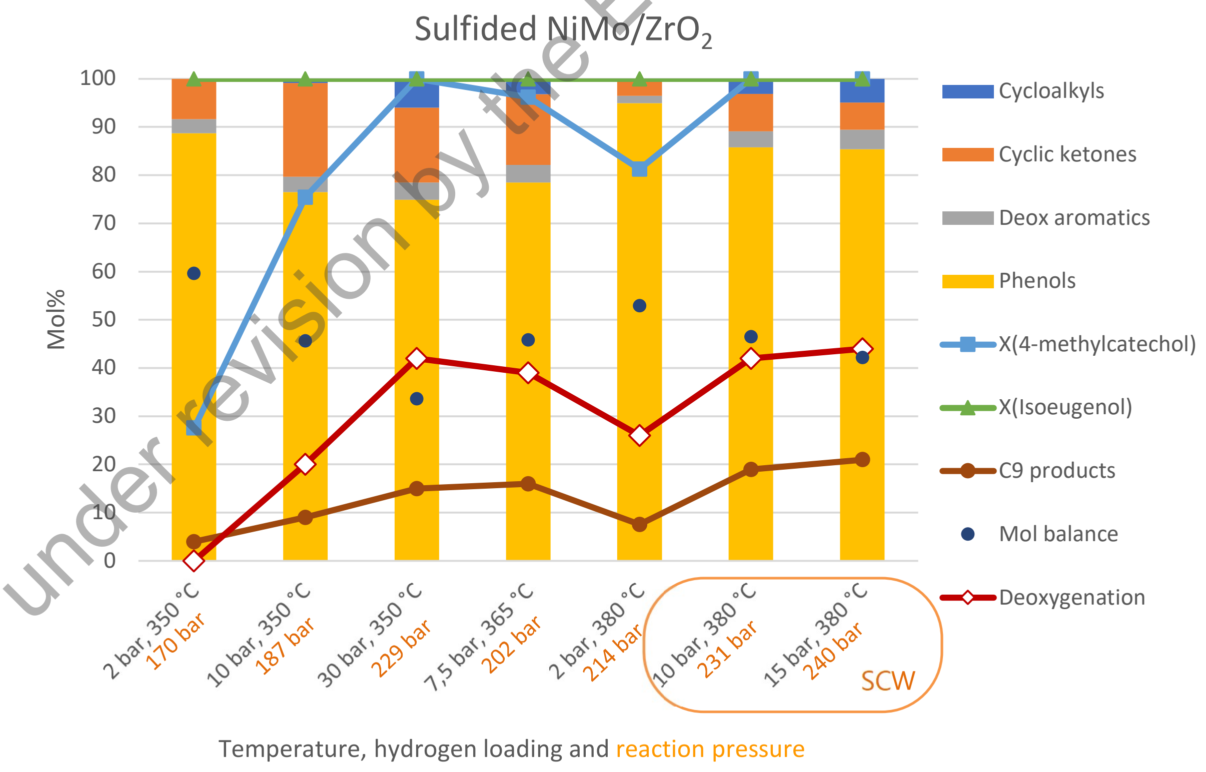


Figure 5. Effect of reaction conditions on model compound HDO with sulfided NiMo/ZrO$_2$ (BLF-03-S).

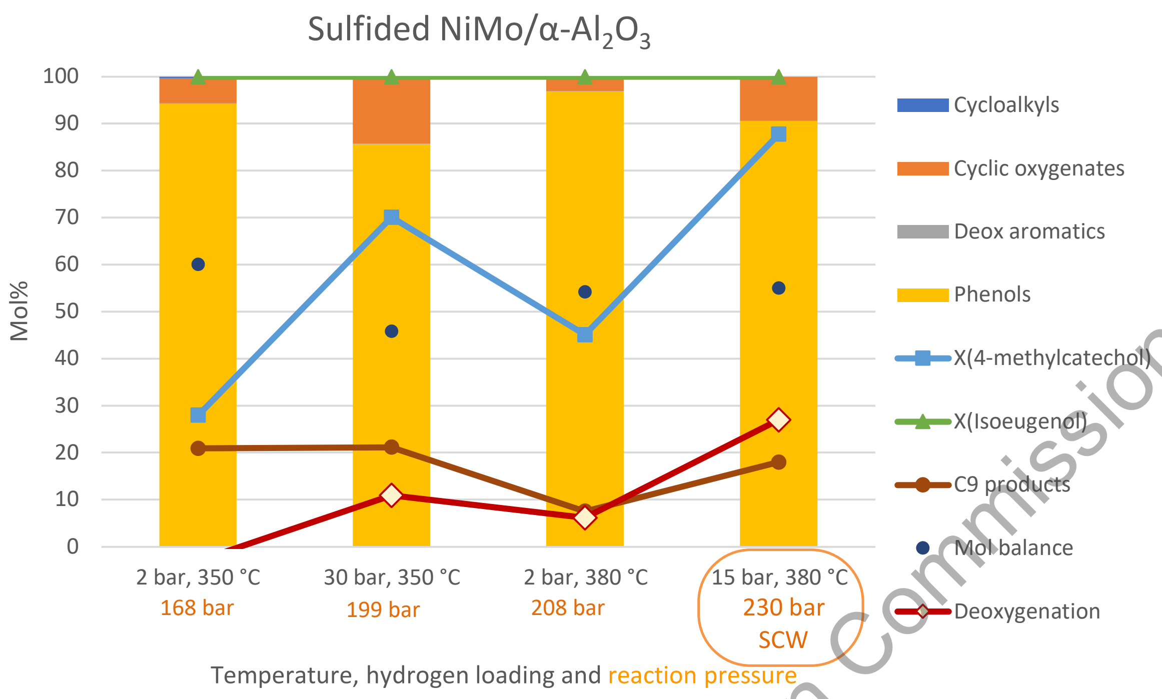


Figure 6. Effect of reaction conditions on model compound HDO with sulfided NiMo/α-Al$_2$O$_3$ (BLF-01-S).

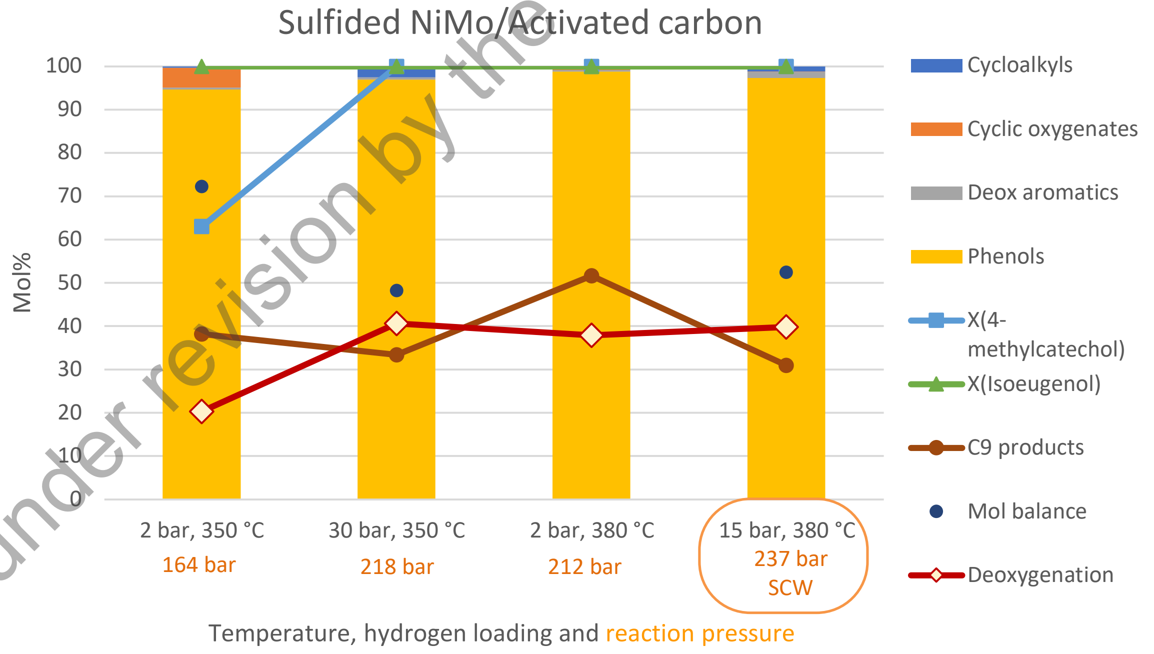


Figure 7. Effect of reaction conditions on model compound HDO with sulfided NiMo/AC (BLF-07-S).

Table 7: Gas phase composition after HDO experiments

Gas composition (vol%)	NiMo/α-Al_2O_3 (BLF-01-S)				NiMo/AC (BLF-07-S)			
	2 bar, 350 °C	30 bar, 350 °C	2 bar, 380 °C	15 bar, 380 °C	2 bar, 350 °C	30 bar, 350 °C	2 bar, 380 °C	15 bar, 380 °C
H_2	92	94	>90	94	85	98	84	95
CO_2	0.15	0.03	0.51	0.06	0.16	0.01	0.50	0.09
CH_4	3.2	0.7	6.5	1.5	3.5	0.5	4.6	1.2
Gas phase C (mol%)	1.8	3.4	3.6	4.3	8.5	7.1	2.5	4.9

The results of the model compound experiments were analysed with MODDE Pro 13.0.2 to determine how the different parameters affect the outcome. Temperature and hydrogen loading were set as quantitative factors, while the catalyst was set as qualitative factor. Figure 8 summarises the effect of the factors on the different responses (results); higher positive bar indicates a stronger positive effect on the response and vice versa. While the quality and reliability of the models could be improved with additional experiments, we think that the analysis nonetheless helps to interpret the results and to compare the effect of the reaction conditions and catalyst on the outcome. Based on the analysis, the reaction parameters have a stronger effect on the MC conversion than the choice of catalyst, even though the alumina supported catalyst shows a negative effect, i.e. lower conversion compared to the other catalysts. Furthermore, supercritical conditions did not show particular benefit in the experiments; similar conversions and DoD could be obtained using e.g. higher hydrogen loading at a lower temperature compared to SCW. Similarly, DoD is strongly affected by the temperature and hydrogen partial pressure. In this case the higher HDO activity of S-NiMo/AC (BLF-07-S) shows as a high positive coefficient, whereas S-NiMo/Al_2O_3 (BLF-01-S) shows a strong negative effect. When comparing the selectivities to the different product groups, the catalysts start to show more differences. For instance, the hydrogenation of the aromatic ring is more pronounced with the titania and zirconia-supported catalysts, the latter of which also shows a strong positive effect on selectivity towards deoxygenated aromatics. However, despite the seemingly strong coefficients, it is worth noting that the overall selectivities to the aliphatic and deoxygenated products were rather low. Interestingly, the carbon-supported catalyst shows positive coefficient only in the selectivity to phenols. According to Zhao *et al.* (2011), the complete hydrodeoxygenation of phenol in aqueous phase requires both active metal and acid sites; carbon-supported metal alone was not active. Based on our results, it could be proposed that the metal oxide support functions as an acid under the hydrothermal conditions, promoting the HDO of phenols. This is supported by the extensive cracking of the C9 backbone, which was especially pronounced with the metal oxide-supported catalysts; cracking is usually promoted by acidic supports.

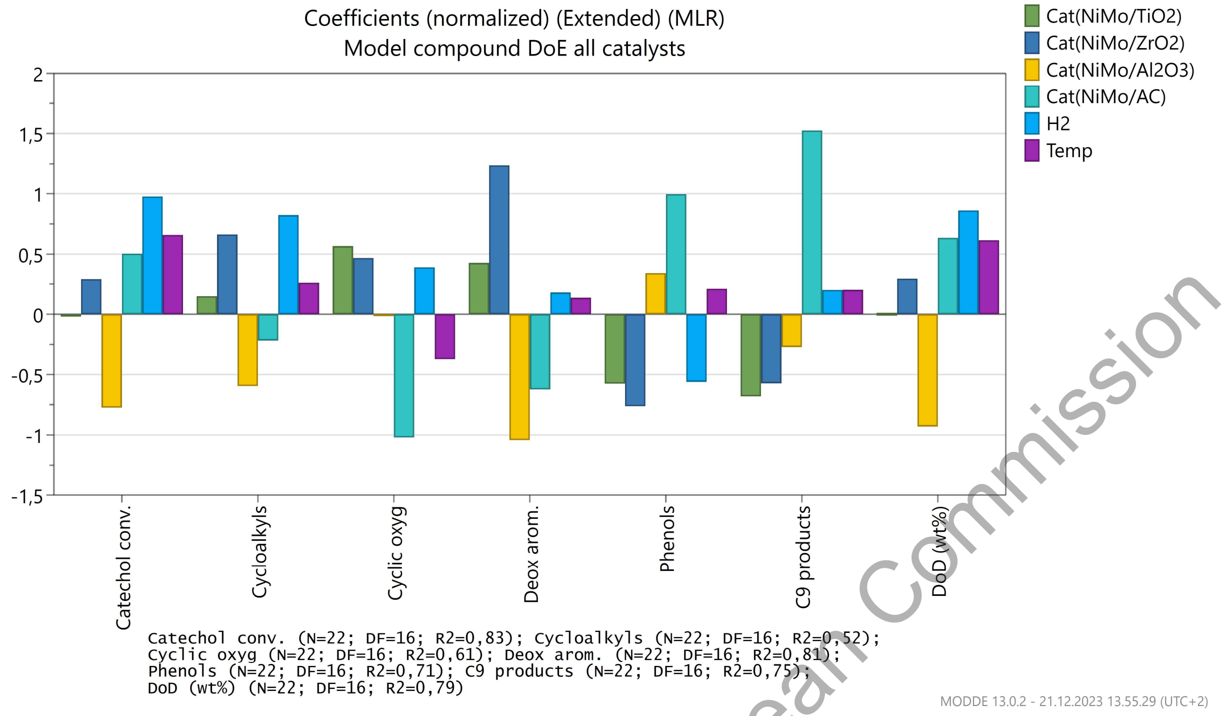


Figure 8. Statistical analysis of the effect of reaction parameters (catalyst, temperature, hydrogen loading) on the HDO of model compounds.

4.2.2. Biocrude upgrading

After the model compound experiments, our intention was to test the IHDO using the real BL-based feedstock from TAU. However, due to the delays in the commissioning of the pilot reactor at TAU, we had to use alternative biocrude to study the hydrothermal HDO. Lignocellulosic (pine) HTL biocrude, obtained from Aarhus University, was selected as the feedstock. The biocrude contained a high amount of solids due to aging, and therefore it was pretreated by dissolving in isopropanol, filtering and evaporating in the rotavap. About 15-30 wt% of the biocrude was removed in the filtration. Table 8 shows the elemental analysis results of the biocude before and after the pretreatment.

Table 8. Composition of the HTL biocrude

Sample	Biocrude yield (wt%)	Elemental composition (%)					H/C ratio
		C	H	N	O	S	
Aarhus HTL biocrude	N/A	62.4	7.7	0.1	29.8	0.009	1.47
Pretreated biocrude*	80	69	8.2	0.1	22.7	0.03	1.56

*Several batches of pretreated biocrude were made, results from one are given here as an example. The upgrading results were calculated using the corresponding batch.

The first experiments with the biocrude were carried out to compare different catalysts in the hydrothermal HDO. The best-performing catalyst, S-NiMo/AC (BLF-07a-S), was selected based on the model compound experiments. In addition, ruthenium-based catalysts were selected after successful tests in the continuous flow experiments at PSI; a sulfur-treated S-Ru/AC showed promising stability and activity in the hydrodeoxygenation of isoeugenol (Chapter 5.2.2). As a comparison, untreated Ru/AC was also used. The experiments were run at subcritical conditions using hydrogen partial pressure of 30 bar at RT at 320 °C for 3 h. Lower temperature was applied here to show the differences in catalyst activity clearer. In the first experiment with S-Ru/AC, the mass balance is low due to incomplete recovery of the viscous bio-oil from the reactor. In the following experiments, the produced bio-oil was separated from the reactor by extraction with ethyl acetate. All the fractions were analysed to determine the mass and carbon balances and the composition of the products; Figure 9 shows the carbon balance of different product fractions. The yield of the bio-oil was around 55%, and significant amounts of coke were also produced, around 30%. The aqueous phase contained about 10% of the biocrude carbon, and a small amount was detected in the gas phase. According to analysis of the bio-oil, the oxygen content was at similar level as with the pretreated biocrude, around 22%, and low DoD:s were observed (up to 10%) (Table 9).

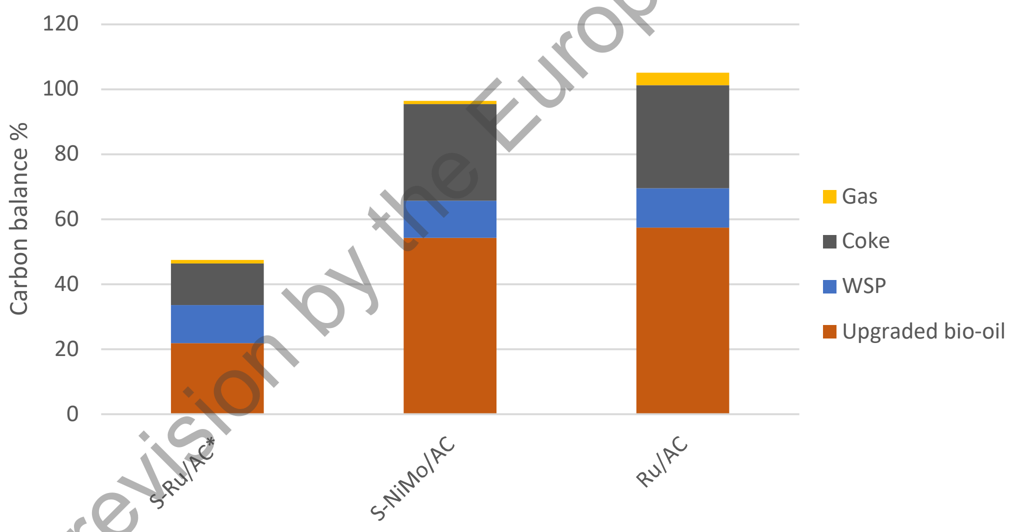


Figure 9. Carbon balance of catalyst comparison experiments in biocrude upgrading. *Lower carbon balance due to different workup procedure.

Table 9. Bio-oil properties in comparison of different catalysts.[a]

Catalyst	Bio-oil yield (wt%)	Elemental composition (%)					H/C ratio	DoD (%)	Pressure at temp. (bar)	ΔP (bar)
		C	H	N	O	S				
Pre-treated biocrude*	N/A	69	8.2	0.1	22.7	0.03	1.56	N/A	N/A	N/A
S-Ru/AC	>23.3[b]	68.2	8.3	0.1	23.4	0.02	1.45	1.3	163	-2
S-NiMo/AC	52.9	69.4	8.1	0.1	22.4	0.02	1.39	5.6	160	-3
Ru/AC	55.9	70	8.7	0.1	21.2	0.02	1.48	10.6	152	-5

[a] Reaction conditions: 25 g pretreated biocrude, 125 g water, 10 wt% catalyst, 30 bar H_2 (RT), 3h at 320 °C. [b] Incomplete recovery

As a next step, we wanted to examine the effect of the process conditions, i.e. subcritical vs supercritical, on the HDO performance. Simultaneously with the studies in batch conditions, PSI studied the continuous flow stability of the catalysts. Based on the results, the stability of the sulfur-treated S-Ru/AC was superior to all of the tested catalysts, and therefore it was chosen for the further testing in batch experiments with the Aarhus biocrude. The effect of parameters was studied with temperature ranging from 320 to 380 °C, hydrogen loading from 5 to 15 bar and reaction time from 2 to 4 h. The temperature range was increased from the model compound studies to cover a wider range of conditions. The carbon balances of the experiments are shown in Figure 10, the total carbon balance amounting to 40-100%. It should be noted that especially the supercritical conditions were very challenging to the reactor, and several leakages occurred resulting in reduced mass and carbon balances and/or the need to repeat experiments. Therefore, the most reliable results are those with carbon balance above 80%. The Figure 10 and Table 10 also show the results from some of the unsuccessful runs to give an idea on how the reduced pressure affects the outcome.

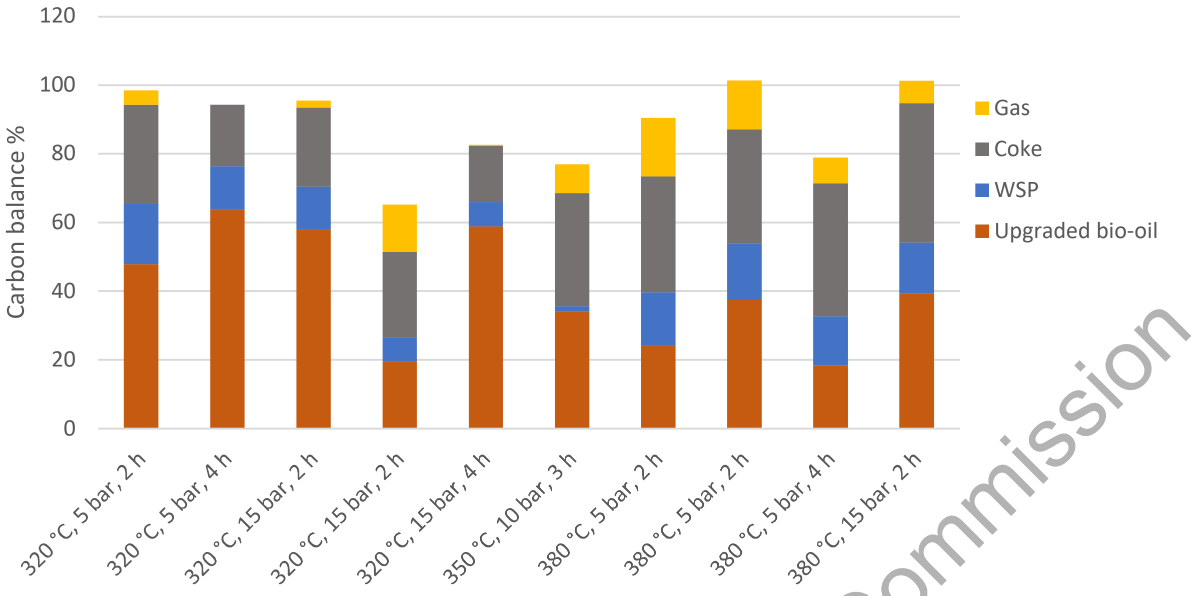


Figure 10. Effect of reaction conditions on the carbon balance of the biocrude HDO using S-Ru/AC.

At 320 °C, the yield of the bio-oil ranged from 46 to 63 wt% in the more successful experiments (Table 10). In terms of carbon balance, the bio-oil contained between 48-64% of the biocrude carbon. Increasing the time or hydrogen loading seemed to have an increasing effect on the bio-oil yield. A significant amount of coke, between 18-29 C% formed in the HDO reaction. The aqueous phase contained up to 20% of the biocrude carbon. According to GC-MS analyses, the most abundant compounds in the aqueous phase were isopropanol and acetone, originating from the pretreatment of the biocrude and the subsequent dehydrogenation, respectively. Other compounds identified in the aqueous phase were aliphatic alcohols, phenols and cyclic oxygenates similar to those detected in the model compound experiments. Increasing the temperature to 380 °C seemed to decrease the bio-oil yield and increase the coke amount; up to 41% of the carbon ended up in the coke. Furthermore, the amount of gaseous products increased to up to 17 C% at 380 °C. The oxygen content of the bio-oil was above 20% in all experiments, and the fluctuation of the DoD was so high (between -8 and 10%) that clear conclusions are difficult to make about the effect of the process conditions on the HDO performance.

Table 10. Bio-oil properties in screening of process conditions with S-Ru/AC catalyst.

Conditions (T, H_2 loading, time)	Bio-oil yield (wt%)	Elemental composition (wt%)[a]				H/C ratio	DoD (%)	Pressure at temp. (bar)[b]	ΔP (bar)[c]
		C	H	N	O				
320 °C, 5 bar, 2 h	45.6	69	8.2	0.1	22.7	1.42	9.9	N/A[d]	N/A
320 °C, 5 bar, 4 h	63.2	67.6	8	0.1	24.3	1.51	1.6	119	-6
320 °C, 15 bar, 2 h	55.6	68.2	8.1	0.1	23.6	1.48	6.3	111	+26
320 °C, 15 bar, 2 h	*19.7*	*68.6*	*8.9*	*0.1*	*22.4*	*1.56*	*4.7*	*130*	*-22*
320 °C, 15 bar, 4 h	60.1	65.6	8.3	0.1	26	1.55	-5.3	128	+4
350 °C, 10 bar, 3 h	34.9	64.8	8.7	0.1	26.4	1.68	-4.8	159	-1
380 °C, 5 bar, 2 h	23.8	69.4	9	0.1	21.5	1.42	8.5	192	+3
380 °C, 5 bar, 2 h	37.5	65.9	8.9	0.1	25.1	1.6	0.4	201	+4
380 °C, 5 bar, 4 h	*19*	*66.9*	*9.2*	*0.1*	*23.8*	*1.6*	*-4.4*	*202*	*-21*
380 °C, 15 bar, 2 h	41	66.2	8.9	0.1	24.8	1.61	-8.8	224	-1

Reaction conditions: 25 g pretreated biocrude, 125 g water, 10 wt% catalyst. The experiments which showed significant leakage are marked in *Italics*. [a] Sulfur content 0.02 in all experiments. [b] Pressure when the reaction temperature was reached. [c] Change of pressure from start to the end of the reaction. [d] Pressure readings not available due to malfunction.

5. Continuous flow experiments

5.1. Experimental

5.1.1. Materials

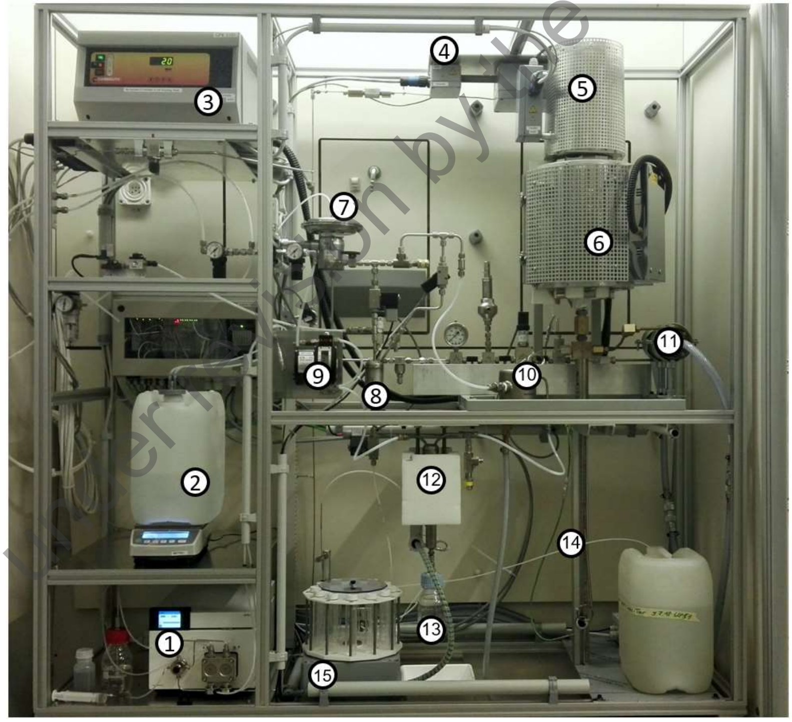
Isoeugenol (>98%, mixture of *cis*- and *trans*), isopropanol (>98%) and DI water was used for the feed preparation. Acetonitrile (MS grade) was used for the GC-FID sample preparation. A variety of individual compounds was used for the GC-FID calibration as received from the supplier.

5.1.2. Catalyst sulfidation

The catalyst sulfidation was performed in a batch reactor under H_2 atmosphere. In a standard procedure a 56 mL batch reactor was filled with 6 g of catalyst, 6.15 mL of n-hexane and 2.15 mL of DMDS. The sealed reactor was flushed three times with 30 bars Argon and pressurized to 30 bars in hydrogen. The sulfidation was performed at 350 °C for 4 h. The sulfided catalysts were stored under n-hexane in an Ar-flushed container.

5.1.3. Experimental setup

All continuous flow experiments were performed in a Konti-I test rig (Figure 11). This test rig allows performing catalytic tests at temperatures up to 450 °C and pressures up to 350 bar with a continuous feed flow in the range from 5 to 50 mL/min.



1	HPLC Pump
2	Feed tank, Balance for mass flow calculation, suction lance with level switch
3	Carbolite oven controller
4	Preheater
5	Transfer heater
6	Carbolite oven
7	Pressure regulator
8	Sample extraction
9	Product gas flow transmitter recorder
10	Phase separator (V_{liq} = 160 mL))
11	Product cooler
12	Gas cooler (cold trap)
13	Condensate container
14	Temperature lance scale
15	Auto sampler

Figure 11. Konti-I experimental test rig

The feed was pumped into the system with a high-pressure pump (Knauer 80P). The mass flow rate was controlled with a balance (Mettler Toledo). The feed was heated to reach desired temperature at the entry of the catalyst bed with a series of three heaters: pre-heater and transfer heater upstream of the catalytic reactor, followed by a tube furnace around the tubular reactor (Carbolite). The fixed-bed plug-flow reactor (L = 460 mm, i.d. = 13 mm), made of 316L stainless steel (SITEC-Sieber Engineering AG), was filled with a catalyst (1–5 g). α-Al_2O_3 beads (0.8 mm diameter, 0.03 $cm^3\ g^{-1}$ porosity, Alfa Aesar) were loaded upstream of the catalyst bed, acting as an inert filling material. The feed descended into the reactor, passing first through the inert filling material and subsequently traversing the catalyst bed prior to exiting the reactor. The packed bed within the tubular reactor was positioned at a desired elevation using stainless steel wire mesh of three different sizes: 0.08, 0.16, and 0.25 mm. The reactor effluent was cooled down with a heat exchanger and forced through a 15 μm frit to protect the valves downstream. A back pressure regulator (Tescom) maintained the system at the desired pressure (25-30 Mpa). The reactor effluent eventually entered a phase separator, from where the liquid products and gas exited the setup. The gas products flowed through a Peltier cooler (1–4 °C) to condense the water out of the gas before being analysed online with a μ GC (Inficon). An automated sampler was used to collect the *in situ* samples at defined experimental conditions.

5.1.4.Model compound experiments

Isoeugenol was chosen as a model compound for the HDO experiments. To obtain a homogeneous feed solution, isoeugenol was first dissolved in isopropanol and, next, added to water yielding a final feed composition of: 5 % isoeugenol : 35 % iPrOH : 60 % H_2O. Such high isopropanol concentration is required to maintain a good solubility of the isoeugenol. At the same time, isopropanol serves as an *in situ* H_2 source. All experiments were performed in a stainless steel fixed-bed plug-flow reactor (i.d. = 13 mm). 5 g of a catalyst was used in a standard experiment (c.a. 6 cm bed height) and the rest of the reactor was filled with inert 0.8 mm α-Al_2O_3 beads. Blank experiments were performed by feeding 35 % iPrOH in water and 5 % isoeugenol : 35 % iPrOH in water over a reactor filled with α-Al_2O_3 beads. The influence of the reaction temperature (365 – 415 °C), pressure (25 – 30 MPa) and space velocity (400 – 8000 $g_{Org}\ g^{-1}\ h^{-1}$) on the catalytic activity was evaluated.

The gaseous products were analyzed online with a micro-GC. The liquid products collected *in situ* under defined set of experimental conditions (T, P, WHSV) were analyzed with GC-FID and GC-MS.

5.2. Results

5.2.1.Metallic catalyst

First, a blank experiment with 5 % isoeugenol : 35 % iPrOH in water but without a catalyst was performed to discriminate any possible influence of the reactor for the catalyst activity. The blank experiments revealed that i) hardly any gas was produced under SCW conditions without a catalyst and ii) only small amount of dihydroeugenol was present in the products. Those results indicate a high stability of isoeugenol and isopropanol in SCW.

Due to the instability of the NiMo-based catalysts under the continuous SCW flow, all HDO experiments were performed with Ru/AC (RCAT®-8830) catalyst. At first, the catalytic activity of the as received metal Ru/AC was evaluated. Note that the as-received catalyst is passivated, meaning a ca. 1.5nm layer of Ru(IV) oxide is present at its surface. RuO_2 gets nearly fully reduced in the presence of light alcohol at temperature as low as 200°C (Dreher, 2013).

The gas production rates over Ru/AC catalyst are presented in Figure 12. As expected, Ru/AC was found to be very active towards SCW gasification in the presence of isopropanol. However, the introduction of isoeugenol to the system strongly inhibited the gasification efficiency of the catalyst. This phenomenon can be possibly explained by the covering of the Ru sites by the aromatic rings from the isoeugenol and/or by the formation and deposition on Ru surface of polyaromatic compounds (coke).

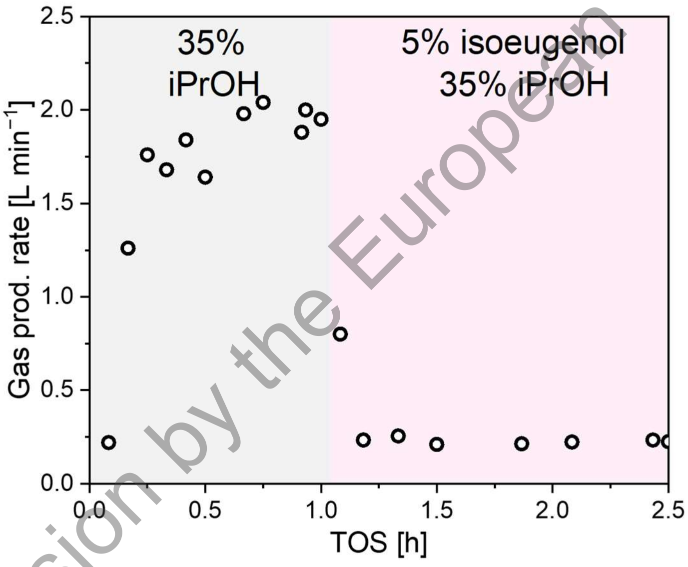


Figure 12. Gas production rate during the isoeugenol HDO over the Ru/AC catalyst (WHSV = 8000).

The analysis of the gases produced revealed CH_4 and CO_2 being the main components (Figure 13). The gas composition observed with isopropanol with and without isoeugenol were very similar. Additionally, the gas mixtures contained up to 10 % of H_2. This observation confirmed the possibility to produce H_2 *in situ* under the experimental conditions. The gas balance was not fully closed (ca. 10-15 %) most probably due to insufficient calibration of volatile organic C_2-C_x compounds and presence of H_2O residuals.

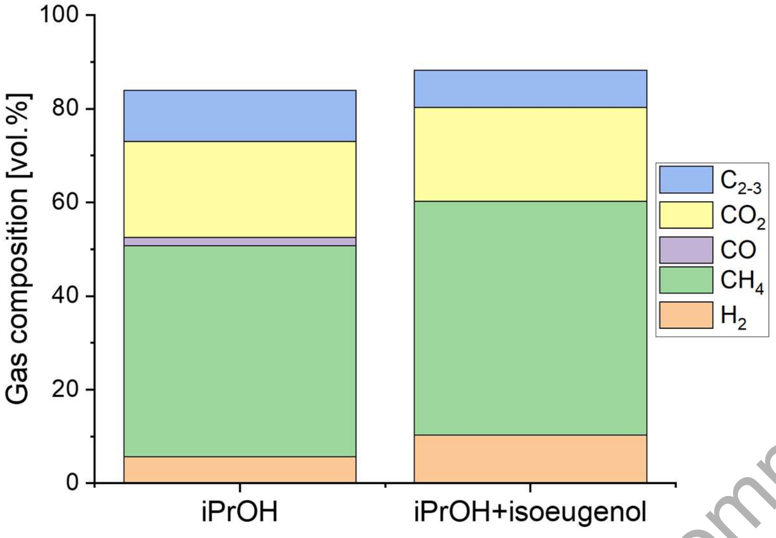


Figure 13. Composition of the gas products during the isoeugenol HDO over the Ru/AC

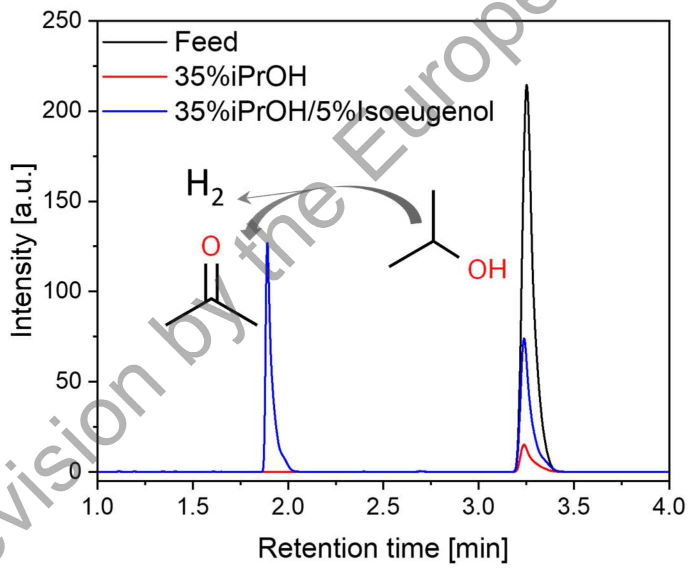


Figure 14. GC-FID signal of isopropanol and acetone in the liquid products during the isoeugenol HDO over the Ru/AC.

The analysis of liquid products revealed that when only isopropanol in water is fed to the system, isopropanol is almost fully gasified (Figure 14, red line) and no additional peaks are observed on the chromatogram. However, when isoeugenol was introduced to the feed a very different chromatogram was obtained. The peak of isopropanol was higher, in phase with a lower gas production, but in particular a peak corresponding to acetone was observed. The peak area indicates that most of the isopropanol was dehydrogenated to acetone, releasing H_2 to the system and only less than 30 % of isopropanol being gasified. A further analysis of the liquid products chromatograms reveled that at very high space velocity (8000 g_{Org} g^{-1} h^{-1}), isoeugenol is not fully converted (Figure 15). At the space velocities below 1600 g_{Org} g^{-1} h^{-1} the conversion of isoeugenol reaches 100 %. However, dihydroeugenol was found to be the main product at WHSV = 1600 g_{Org} g^{-1} h^{-1} indicating that only double bond hydrogenation but no deoxygenation occurs under these conditions. To shift the rection further towards the deoxygenation, the space velocity was reduced to 400 g_{Org} g^{-1} h^{-1}. Indeed, it was found that the intensity of the dihydroeugenol peak reduced significantly at low space velocity. Instead, multiple peaks of mostly phenolic compounds can be observed on the GC-FID chromatogram with 4-propylphenol being the main product (Figure 16).

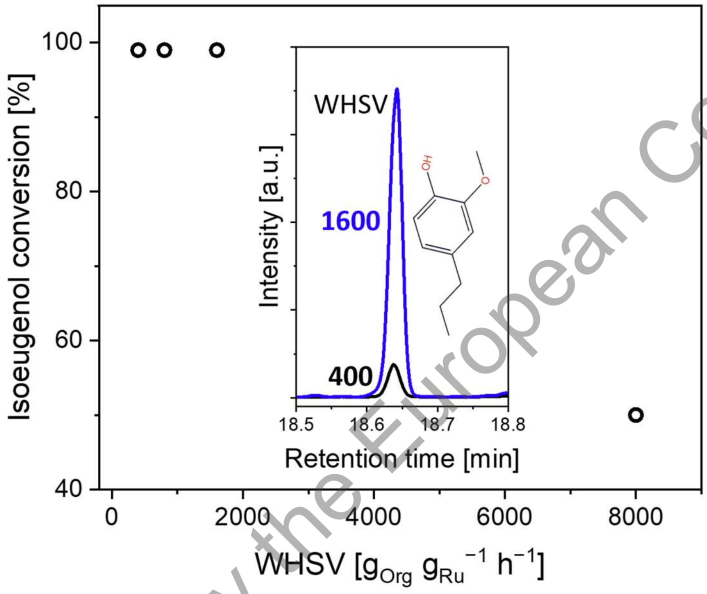


Figure 15. Influence of the WHSV on the isoeugenol conversion over Ru/AC. GC-FID peak of dihydroeugenol is shown in the inset.

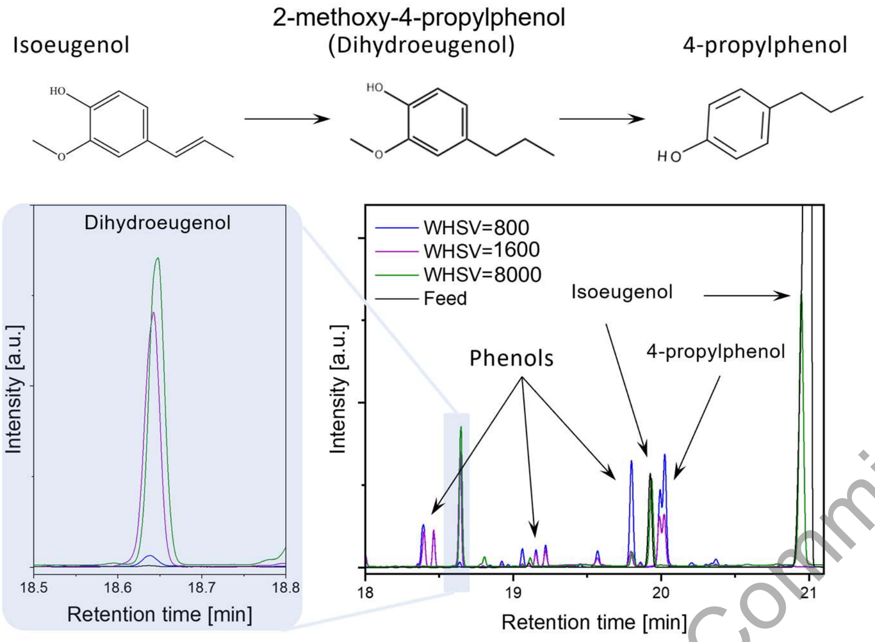


Figure 16. Influence of the WHSV on the liquid products.

5.2.2.Sulfided catalyst

In the next step we wanted to investigate the influence of sulfur on the catalyst activity. This is a very important step as a real BL-based feedstock, e.g. the desalinated stream coming from the salt separator, is S-rich. Notably, it was proved to contain a substantial amount of organosulfur compounds (deliverable D1.2), which are known to poison efficiently Ru-based catalyst under these conditions (Dreher, 2013).

For those experiments Ru/AC was preliminary fully sulfided using the procedure described above to obtain S-Ru/AC. A preliminary test revealed a high stability of S-Ru/AC catalyst under SCW conditions even with a S-free feed. However, to eliminate any possible S-leaching during experiments, 1000 ppm DMDS was introduced to the feed. The gas production rate and gas composition as a function of WHSV during the hydrothermal gasification of isopropanol with and without isoeugenol is presented in Figure 18. As expected, S-Ru/AC was found to have a much lower gasification activity for SCWG of isopropanol as compared to S-free Ru/AC. That may be explained by the sulfur poisoning of Ru being one of the main deactivation mechanisms in SCWG (Dreher, 2013). However, despite a saturation of the catalyst with sulfur, the gas production rate with isopropanol only was about 35 % that of the S-free catalyst, which is higher than one would expect. Additionally, it was found that the produced gas consisted mainly of C_2-C_3 compounds with ca. 10 % of H_2 (Figure 17), which probably explains the difficulty to close the gas balance as a few organic C_2-C_4 gases were calibrated. The introduction of isoeugenol to the feed changed the gas composition significantly. It was observed that a significant amount of H_2 (23 to 60 %) was produced, probably mostly *via* dehydrogenation of isopropanol to acetone. In parallel, the absolute gas production rate was observed to decrease linearly with decreasing WHSV at values equal to or lower than 800 $g_{Org}\ g^{-1}\ h^{-1}$. Moreover, it was found that WHSV influence the gas products dramatically, i.e. increasing the WHSV from 800 to 1600 g_{Org} g^{-1} h^{-1} resulted in doubling the concentration of H_2 (up to ca. 60 %). However, the higher concentration of H_2 in the gas products does not necessarily indicate a higher *in situ* H_2 production rate, but is rather an indication of a lower H_2 "consumption" during the hydrogenation/hydrodeoxygenation of isoeugenol at high WHSV. Overall, the significant amount of H_2 produced *in-situ* from isopropanol over sulfided S-Ru/AC makes the alcohols, present in black liquor and produced from the HTL of BL (see deliverable D1.2), a useful source of H_2.

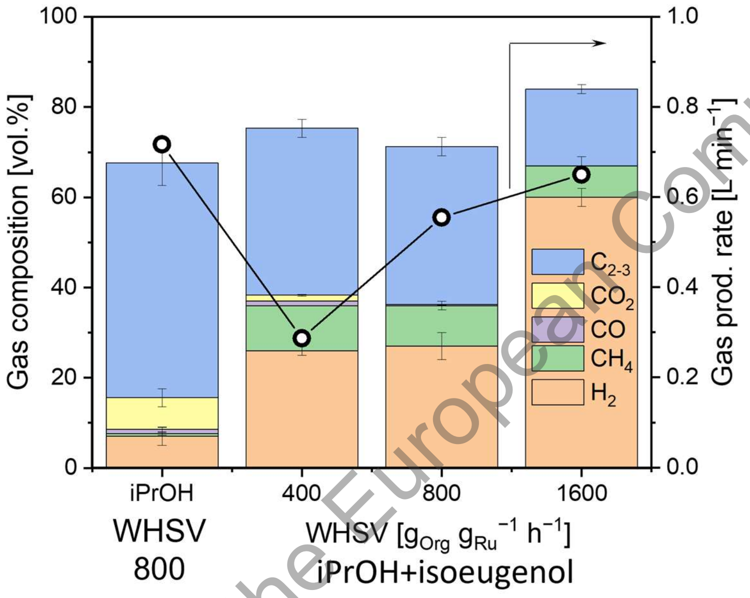


Figure 17. Gas production rate and composition of the gaseous products during the isoeugenol HDO over the S-Ru/AC as a function of WHSV.

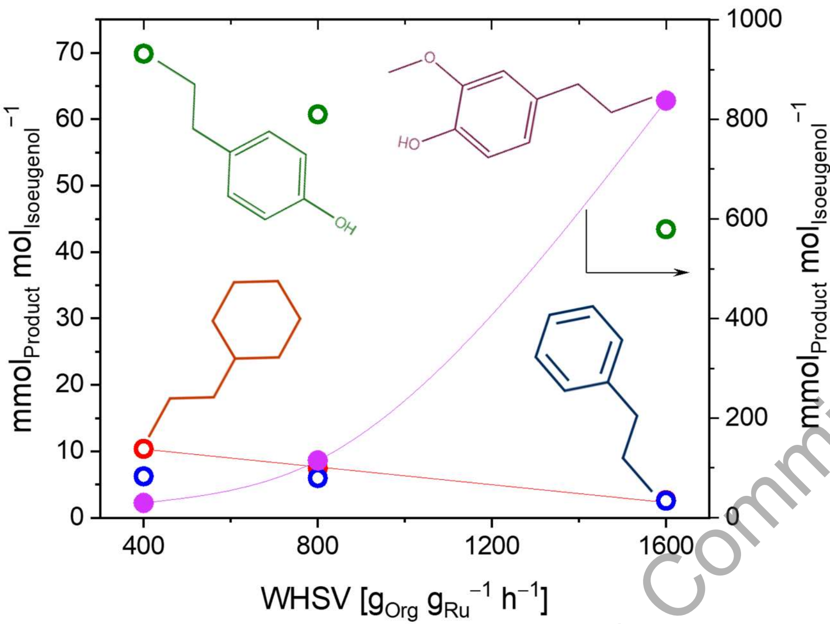


Figure 18. Effect of the WHSV on the main C9-C10 yield during the HDO of isoeugenol over S-Ru/AC.

The liquid products obtained during the HDO of isoeugenol over S-Ru/AC under various conditions were also analysed *via* GC-FID. A large number of peaks was observed on the chromatograms. Due to the complexity of the system and presence of isomers, not all of the compounds were properly identified and calibrated. Here we focused on the C_9-C_{10} compounds as the targeted products of the HDO of isoeugenol. The GC-FID analysis of the liquid products revealed that dihydroeugenol is the main product at high space velocity (1600 g_{Org} g^{-1} h^{-1}), as observed with the metallic Ru/AC. As expected, the reaction was shifted forward to deoxygenation with a reduction of space velocity. In particular, it was found that while the selectivity towards dihydroeugenol at WHSV = 1600 g_{Org} g^{-1} h^{-1} was 80 %, this value decreased to less than 3 % at WHSV = 400 g_{Org} g^{-1} h^{-1} (Figure 18).

Remarkably, completely deoxygenated C_9 compounds, i.e. propylbenzene and propylcyclohexane, were detected in the liquid products using the sulfided S-Ru/AC, while none was formed with S-free Ru/AC. Additionally, partially deoxygenated C_9 compounds such as 4-propylanisole and 4-propylphenol were detected. Though, the observed yields of deoxygenated C_9 compounds were not very high, they increased with the reduction of WHSV. Due to the limitation of the experimental setup, it was not possible to further reduce the WHSV of the reaction.

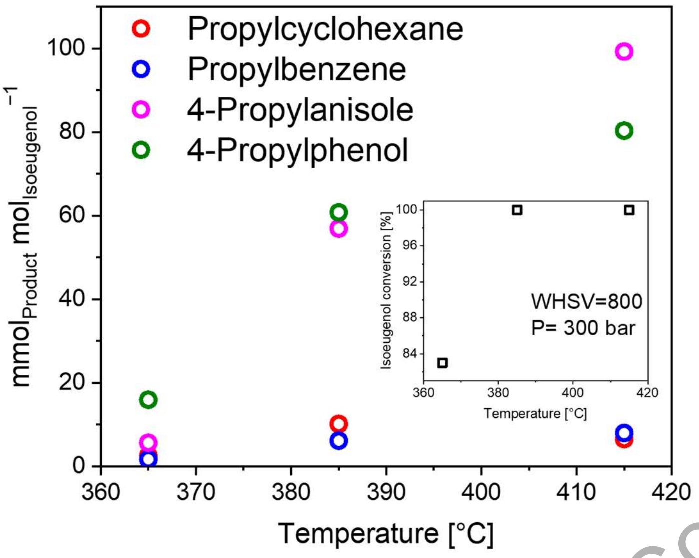


Figure 19. Effect of the reaction temperature on the main C9 deoxygenation products yield during the HDO of isoeugenol over S-Ru/AC. Isoeugenol conversion is shown in the inset.

To further optimize the reaction conditions, we evaluated the influence of the reaction temperature and pressure on the catalytic activity. First, the temperature was varied from 365 °C to 415 °C (P = 300 bar, WHSV = 800 g_{Org} g^{-1} h^{-1}) to cover sub- and supercritical conditions (Figure 19). It was found that at 365 °C the isoeugenol was not fully converted with ca. 15 % being unreacted. At higher temperature, conversion reached 100 %. Moreover, the yield of deoxygenated C_9 compounds was found to increase significantly with increasing temperature. A similar observation was made for the reaction pressure, i.e. a better catalyst performance was obtained at higher pressures. In particular, the isoeugenol conversion and the yield of DO compounds were twice higher at 300 bars as compared to 250 bars (T = 400 °C, WHSV = 1600 g_{Org} g^{-1} h^{-1}) (Figure 19).

Overall, those findings make S-Ru/AC a promising catalyst for IHDO in SCW conditions. Obtained results suggest that the yield of deoxygenated and hydrogenated compounds can be strongly improved by performing reaction at very low space velocity and temperature above 400 °C. S-Ru/AC was found to be stable under continuous SCW flow conditions with a S-rich feed. Additionally, a very low gas production rate observed during the HDO of isoeugenol indicates that chosen catalyst is highly selective towards liquid products. Moreover, the presence of alcohols in the real BL-based feedstock can be an *in situ* source of H_2 for the HDO reaction possibly allowing to fully or partially substitute the supply of external H_2 consumption in the initially intended project's process.

6. Summary and future prospects

The aim of the Task 3.2.1 was to study the performance and stability of various catalysts in the hydrothermal hydrodeoxygenation of BL-derived HTL-oil. The task was done in close collaboration with the catalyst development Task 3.1. This report summarises the work done on testing the stability and activity of the catalysts in the hydrothermal IHDO both in batch and continuous reactor systems. Due to the delays in commissioning the TAU HTL-pilot reactor, the HDO experiments were carried out mainly using model compounds, selected based on the findings in WP1, and lignocellulosic HTL biocrude obtained from Aarhus university.

Hydrothermal conditions are known to be detrimental for many common catalyst supports and metals, and therefore the stability of the catalysts was tested rigorously. Based on stability tests in supercritical water in batch mode, α-alumina, titania and activated carbon were selected as suitable supports for the catalysts. Sulfided nickel and molybdenum were employed as the active phase and these catalysts were applied in the HDO of model compounds in batch mode.

The activity of the catalysts and the effect of process conditions in batch experiments was studied using isoeugenol and 4-methylcatechol as the model compounds to represent the functionalities in the BL-derived biocrude. While the process conditions, i.e. temperature and hydrogen loading, had a strong effect on the outcome of the reaction, phenols were the main products in all cases, indicating that full deoxygenation is difficult under the aqueous conditions with NiMo-based catalysts in batch mode.

In parallel, stability tests in a continuous flow reactor showed extensive leaching of the active metals in the NiMo catalysts, contrary to the stability tests in batch mode. Therefore, ruthenium-based catalysts were used to continue the work on the hydrothermal HDO of HTL biocrude. In the absence of the BL-based feedstock from TAU, lignocellulosic HTL biocrude from Aarhus University was applied as a model feed for the biocrude upgrading experiments. The biocrude was rather viscous and aged, and pretreatment to remove the solids was necessary prior to the upgrading experiments. Due to difficulties with solubility and pumpability, experiments with the biocrude were carried out only in batch mode. Temperature and hydrogen loading were varied to study the hydrothermal HDO both in subcritical and supercritical regime. Using a sulfur-treated ruthenium catalyst, the yields of the upgraded bio-oil varied between 40-60 wt%, and significant amounts of coke were formed (20-40 wt%). Interestingly, coking was highest in the experiments in SCW. Furthermore, the degree of deoxygenation remained rather low (maximum 10%) in all experiments, and the highest DoD, along with the highest bio-oil yield, was observed below the critical point. However, difficulties to dissolve the aged biocrude, as well as the age and non-representative composition of the crude (oligomerised/condensed organics) might have affected the results, as well as the slow heating ramp of the feedstock, known to favor coke formation, inherent to batch reactor.

In continuous mode, isoeugenol was used as the model compound in a mixture of isopropanol and water. Due to the extensive leaching of the NiMo-catalysts in the continuous flow reactor, ruthenium supported on carbon was applied to overcome the issues in stability. It was found that a sustainable amount of H_2 is produced *in situ* from isopropanol indicating the potential of alcohols in the real BL-based feedstock being an *in situ* source of H_2 for the HDO. Reaction temperature and WHSV had a strong influence on the yields of deoxygenated products; the yields of DO compounds increased with reaction temperature and decreased with WHSV. The effect of sulfur (0 to -II), which is present in the IHDO stream (desalinated stream from the IHTL of BL), was studied by treating the Ru/AC catalyst with sulfur compounds both in continuous and batch experiments. Remarkably, the sulfur-treated S-Ru/AC showed very high stability and a good activity in hydrodeoxygenation. Completely deoxygenated C_9 compounds such as propylbenzene and propylcyclohexane were detected in the liquid products, indicating that S-Ru/AC is a promising catalyst for IHDO in SCW conditions.

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